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# Burial metamorphism in Plio-Pleistocene sediments of the Colorado River delta

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# BURIAL METAMORPHISM IN PLIO-PLEISTOCENE SEDIMENTS OF THE COLORADO RIVER DELTA

by

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Burial Metamorphism in Plio-Pleistocene Sediments of the Colorado River Delta
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Mudrocks and fine-grained sandstones from three wells in the Plio-Pleistocene Colorado River delta in the Imperial Valley, southern California, were examined by X-Ray powder diffraction methods, chemical analysis, and scanning electron microscopy to determine the course and extent of low temperature metamorphic reactions in the sediments. This sequence was compared to Tertiary rocks from the U.S. Gulf Coast in an effort to explore the kinetics of low temperature reactions in natural systems.

Mineralogical changes observed are (1) the progressive transformation of mixed-layer illite-smectite to pure illite over the temperature range, 68° C to 210° C, (2) the appearance of chlorite as a diagnetic mineral at 180° C to 194° C, temperatures coincident with the onset of R3 ordering in the illite-smectites, (3) the loss of kaolinite above approximately 210° C, and (4) a progressive decrease in the amount of detrital potassium feldspar over the same temperature interval that brackets the illitization reaction.

Comparison of bulk chemical analyses with analyses of the < 0.1-μm fraction indicates that the clay mineral reactions occur as a result of redistribution of components from the coarse fraction to the fine, clay-rich, fraction.

Comparison of Tertiary sequences with this Plio-Pleistocene sequence confirms that kinetics significantly influence the appearance of clay mineral assemblages at temperatures below approximately 160° C. At temperatures above 160° C, temperature, rather than time, appears to govern the reactions.

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# INTRODUCTION

Low temperature metamorphic reactions in deeply buried pelitic sediments were first observed by Burst (1959) in the Tertiary shales of the U.S. Gulf Coast. He noted a progressive transformation of smectite to illite with increasing burial depth and temperature. Similar changes in clay mineralogy were documented in more detail by Perry and Hower (1970), and Weaver and Beck (1971) in the Gulf Coast; by Dunoyer de Sergonzac (1970) in Upper Cretaceous shales of the African Cameroun; and by Steiner (1968) and Eslinger and Savin (1973) in the volcanic rocks and volcanogenic sediments of the Wairakei and Ohaki-Broadlands geothermal areas of New Zealand.

Hower et al. (1976) summarized the work on low-grade metamorphism of shales and augmented it with a detailed chemical and mineralogical analysis of one burial metamorphic sequence in the Gulf Coast. Hoffman and Hower (1979) explored the use of clay mineral assemblages as geothermometers in the disturbed belt of Montana. Higher grade reactions were reported by McDowell and Elders (1980) in the Plio-Pleistocene sediments of the Salton Sea Geothermal Field. Nadeau and Reynolds (1981) determined the distribution of metamorphic clay mineral assemblages in the Mancos Shale and related their results to the regional tectonics of the southern Rocky Mountains and the Colorado Pleateau.

Although these studies encompass several rock types of different ages in a variety of geologic environments they have in common a regular

progression of clay mineral assemblages that occur at similar temperatures regardless of the setting. As the temperature of a system containing pure smectite and mixed-layer illite-smectite increases the smectite converts to the mixed-layer species and the proportion of illite layers in the mixed-layer illite-smectite increases. This process continues until the percentage of illite layers reaches 100 percent.

As the percentage of illite layers increases three successive ordering schemes are commonly observed. When the proportion of illite layers is less than 65 percent random ordering of expanded and collapsed layers is seen. At greater than 65 percent illite layers a short-range, nearest-neighbor ordering scheme, ISIS, is found. At approximately 85 percent illite layers, long range, Kalkberg-type ordering, IIIS, occurs. (Following the terminology of Jagodzinski (1949) these three ordering schemes are referred to as R0, R1, and R3, respectively.) As temperature continues to increase, a polytypic transformation from 1MD illite to a 2M dioctahedral mica is observed (Maxwell and Hower, 1967).

In the burial metamorphic sequences of the Gulf Coast shales the reaction appears to take place in a system that is closed with respect to all components except $H_2O$, CaO, $Na_2O$ and $CO_2$ (Hower et al., 1976). The potassium and aluminum required by the smectite to illite conversion is derived from the decomposition of detrital potassium feldspar and possibly mica. As the reaction proceeds the percentage of potassium feldspar and mica decreases, $Si^{4+}$ is released and chlorite appears. Hower et al. (1976) conclude that these changes can probably

be represented by the reaction:

Smectite + K-feldspar + Mica = Illite + Chlorite + Quartz

Other work including K-Ar analyses of Gulf Coast shales (Aronson and Hower, 1976) and oxygen isotope studies (Yeh and Savin, 1977; Eslinger et al., 1979) as well as kinetic and thermodynamic investigations (Eberl and Hower, 1976; Eberl, 1977; Eberl, 1978) supports this interpretation.

This paper is based on a detailed examination of cuttings from three wells, Borchard A-1, A-2, and A-3, drilled by the Geothermal Operations Division of Phillips Petroleum Company in the Plio-Pleistocene sediments of the Colorado River delta (Muffler and Doe, 1968) near Brawley, California. Samples from all three wells reflect a monotonous sequence of shales, siltstones and fine-grained sandstones.

Prior to the present study a nearly complete low temperature metamorphic sequence had been observed only in the middle Tertiary sediments of the Gulf Coast (Perry and Hower, 1970; Hower et al., 1976). The percentage of illite layers in mixed-layer illite-smectite in those sequences increases from 20 percent to 80 percent. The present study compares detailed clay mineral assemblages with temperatures in Plio-Pleistocene sediments which exhibit almost the full range of the smectite to illite conversion from > 80 percent smectite layers to pure illite.

A comparison of wells drilled in the Imperial Valley indicates that subsurface mineral assemblages in those wells occur at similar temperatures regardless of burial depth (Muffler and White, 1969; McDowell and Elders, 1980; and this study). Data from Burst (1969) indicates that a significant pressure effect would drive the reaction from illite to smectite. Since the reaction clearly proceeds from smectite to illite, we conclude that the effect of pressure is minor.

Most previous work (e.g. Perry and Hower, 1970; Hower et al., 1976; Hoffman and Hower, 1979) supports the contention that in a single burial metamorphic sequence the progressive appearance of clay mineral assemblages depends on increasing temperature. Nevertheless, at any given temperature the appearance of a particular assemblage is dependent on reaction rate. At the low temperatures encountered in burial metamorphic sequences reaction times may be measured in millions of years. Based on limited Plio-Pleistocene data, Hoffman and Hower (1979) point out that at identical temperatures and similar burial depths Plio-Pleistocene sediments contain a significantly lower-grade clay mineral assemblage than do older Tertiary sediments.

Detailed comparison of the Brawley Plio-Pleistocene sequence with the Tertiary sequence of Hower et al. (1976) illustrates the dual effects of time and temperature on the low-temperature metamorphic reactions that occur in deeply buried sediments.

## Geologic Setting

The Imperial Valley in southern California is a broad depression in the central part of the Salton Trough (Biehler et al., 1964).

Elders et al. (1972) interpreted the anomalously high geothermal gradients within the Salton Trough as evidence for crustal spreading associated with the East Pacific Rise. Local areas of high heat flow such as the Salton Sea and Brawley geothermal fields appear to be associated with Quaternary volcanism (Robinson et al., 1976).

The Salton Trough is filled to a maximum depth of six kilometers (Biehler et al., 1964) with fine-grained sediments of the Colorado River delta. Detailed mineralogical analyses (Muffler and Doe, 1968) indicate that these sediments were derived almost exclusively from the Mesozoic rocks of the upper Colorado River drainage. Deltaic sediments exposed in the Imperial Valley range in age from Late Miocene to Recent and exhibit a similar mineralogical and chemical composition throughout. Equivalent subsurface sections are texturally and chemically, but not mineralogically, identical (Muffler and Doe, 1968).

The Wilson No. 1 well, described by Muffler and Doe (1968), is a few miles southwest of, and somewhat deeper than, the Borchard wells. Lithologies encountered in the Borchard wells are similar to those described by Muffler and Doe for the Wilson No. 1 well. Based on lithologic similarity and proximity of the wells we infer that, like the Wilson No. 1 well, the Borchard wells penetrate sediments that are temporally and compositionally equivalent to the Plio-Pleistocene Palm Springs Formation.

The nearly uniform lithology and restricted age range of this sedimentary sequence makes it ideal for this study. Any mineralogical

changes associated with increased depth and temperature can be attributed to metamorphism rather than to a difference in age or original composition.

## ANALYTICAL METHODS

### Sample Selection

Samples for analysis were selected from cuttings from the three Borchard wells. Well logs were examined to detect any of the problems inherent in the use of cuttings such as sloughing or drilling fluid loss. The cuttings were visually examined for contaminants and washed if necessary.

### Temperature Data

Well temperatures reported in this paper were obtained from the logs of temperature surveys run approximately four months after drilling ended. We feel that this is sufficient time for temperatures to re-equilibrate to a close approximation of pre-drilling conditions.

### Sample Treatment

Samples were crushed in a glazed porcelain mortar and disaggregated in deionized water with an ultrasonic probe. The sample was then separated into > 2-μm and < 2-μm (equivalent spherical diameter) size fractions by repeated centrifugal sedimentation in 250 ml bottles. The < 0.1-μm fraction was separated from the < 2-μm fraction for the Borchard A-2 samples by means of a Sharples continuous flow centrifuge (Jackson 1956).

X-Ray Diffraction Analyses

Oriented samples of the < 2-μm fraction and the < 0.1-μm fraction were prepared for XRD analysis by centrifuging the sample material onto a porous ceramic plate (Kinter and Diamond 1956). Randomly oriented samples of the < 2-μm and > 2-μm fractions were prepared by sprinkling dry powder onto a greased glass slide.

After ethylene glycol solvation, X-Ray diffractograms were run on all oriented samples for the 2θ range, 0° to 32°, using CuK α radiation and a graphite crystal monochromater. Randomly oriented < 2-μm fraction samples were run for the 2θ range, 18° to 40°, to determine illite polytype (Yoder and Eugster 1955; Maxwell and Hower 1967). The randomly oriented > 2-μm fraction was run over the 2θ range, 0° to 65°, to determine gross changes in the overall mineralogy.

The proportion of illite layers in the mixed-layer illite-smectite was determined according to Reynolds and Hower (1970). The position of the $002_{10}/003_{17}$ reflection for randomly interstratified samples and the $005_{27}/002_{10}$ reflection for ordered samples was precisely determined by scanning the 2θ range, 14° to 20°, at 1/4°/min.

The error in Reynolds and Hower's method is generally reported to be ± 5 percent. Srodon (1980) demonstrates the possibility of significantly greater error (15-20 percent) depending on the thickness of the ethylene glycol interlayers. An attempt was made to use the more precise method presented by Srodon (1980). In most cases, however, interference due to the presence of discrete illite in the sample

rendered it useless. For two samples the reflections required by Srodon's method were clear. In both cases Srodon's method gave results that were nearly identical (± 1 percent illite) with the values obtained from Reynolds and Hower's method.

Selected oriented samples were heated at 600° C for one hour. X-Ray diffractograms were then run to detect or confirm the presence of chlorite. X-Ray diffractograms were run on oriented samples previously treated with 1N HCl at 95° C for 90 minutes to confirm the presence of Kaolinite.

## Chemical Analyses

Twenty-four samples from two wells were selected for whole rock chemical analysis. Major element concentrations of the bulk samples were determined by X-Ray fluorescence with matrix effect corrections.

Analysis of the $< 0.1$-μm fraction of twenty-one samples from the Borchard A-2 well was accomplished by atomic absorption spectrophotometry. Samples were fused with lithium metaborate and prepared according to the scheme outlined in Van Loon and Parissis (1966) and Boar and Ingram (1970). The National Bureau of Standards standard reference materials No. 278 and No. 688 were used as standards.

## SEM

Fine-grained sandstones from the sampled intervals were examined primarily to establish the presence of authigenic kaolinite.

# RESULTS

## Mineralogy

X-Ray diffraction analysis of samples from the Borchard wells yields results that are very much in accord with earlier work in deeply buried sediments (e.g., Hower et al., 1976). The six XRD patterns in Figure 1 illustrate mineralogical trends in the < 0.1-μm fraction of selected samples from Borchard A-2. Table 1 presents logged well temperatures and the corresponding illite-smectite mineralogy of selected sample intervals from Borchard A-2.

Smectite to Illite Reaction. The progressive illitization of mixed-layer illite-smectite is the most striking mineralogical change observed in this study. Figure 2 illustrates the variation in illite content of these minerals as a function of increasing temperature.

The sediment near the surface is composed of a heterogeneous mixture of detrital minerals including mixed-layer illite-smectite of varying expansibility and discrete illite. As depth and temperature increase, initial variations in clay mineralogy are eclipsed by the effect of the smectite to illite reaction. The proportion of illite layers in mixed-layer illite-smectite increases in a regular manner until pure illite forms at approximately 210° C.

Ordering of the interlayers progresses from a random, R0, condition at illite percentages below about 65 percent through a partially ordered transition phase to R1 ordering and finally to R3 ordering at illite percentages above 85 percent (Figure 2).

TABLE 1. PERCENTAGE OF ILLITE LAYERS IN ILLITE/SMECTITE, BORCHARD A-2

| Temp. °C | | < 0.1-μm | | < 2-μm |
|---|---|---|---|---|
| 39° | | 36 (2)* | | 32 (5) |
| 48° | | 32 (3) | | 24 (3) |
| 68° | | 13 (2) | | 0 (1) |
| 85° | R0 | 20 (2) | | 13 (4) |
| 105° | | 44 (2) | | 32 (2) |
| 122° | | 50 (2) | | 46 (2) |
| 129° | | 63 (2) | | 53 (2) |
| 138° | R0/R1** | 73 (2) | | 70 (3) |
| 143° | | 75 (2) | | 67 (2) |
| 153° | | 82 (2) | | 78 (2) |
| 160° | R1 | 85 (2) | R1 | 79 (3) |
| 167° | | 91 (2) | | 78 (2) |
| 176° | | 90 (2) | | 85 (6) |
| 180° | R3 | 91 (2) | R3 | 90 (2) |
| 194° | | 93 (3) | | 94 (3) |
| 208° | | 99 (4) | | 96 (4) |
| 220° | | 100 | | 100 |
| 233° | illite | 100 | illite | 100 |
| 247° | | 100 | | 100 |
| 260° | | -- | | 100 |
| 273° | | 100 | | 100 |
| 282° | | -- | | 100 |

* Figures in parentheses indicate maximum probable error.

** R0/R1 designates the partially ordered transition phase.

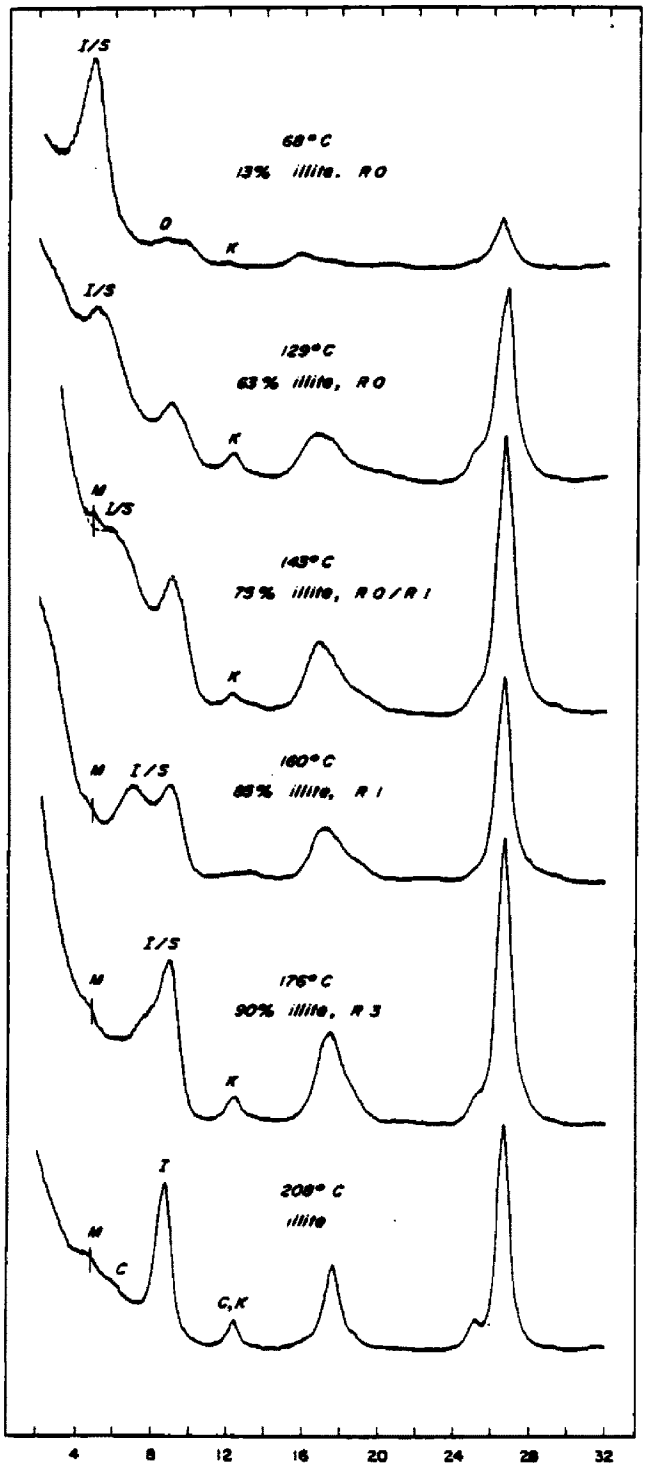


Figure 1. X-ray powder diffraction patterns of glycolated < 0.1-μm fraction samples from Borchard A-2. M = machine artifact. I/S = illite-smectite. D = discrete illite. I = illite. C = chlorite. K = kaolinite.

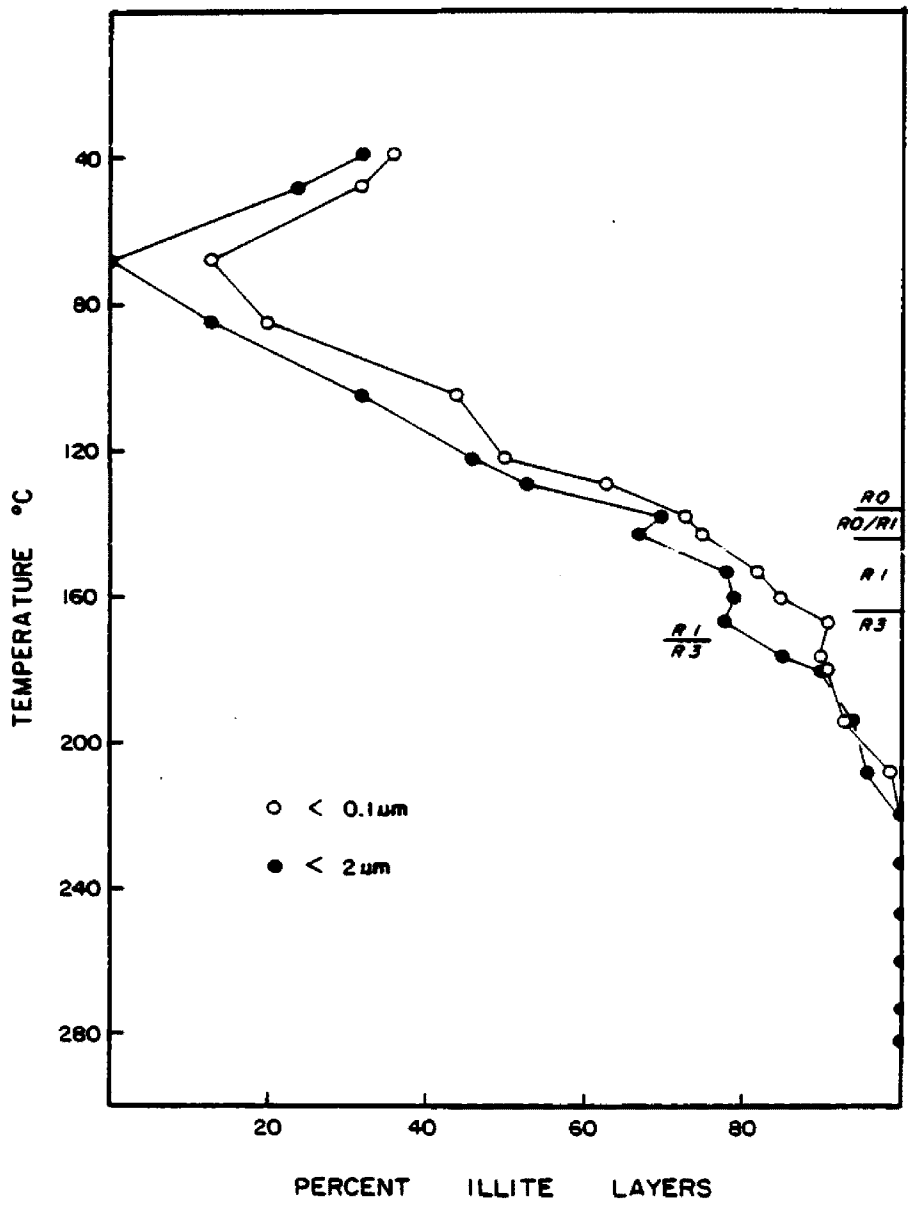


Figure 2. Percentage of illite layers in mixed-layer illite-smectite plotted against logged well temperatures, Borchard A-2. Sample size fractions as indicated. Note that R1 to R3 transition occurs at slightly higher temperatures in the coarser size fraction.

XRD patterns of randomly oriented samples of the < 2-μm fraction suggest that a polytypic transformation of illite from 1Md to 2M takes place at temperatures between 210° C and 300° C. That temperature range is consistent with the results of Yoder and Eugster (1955), Velde and Hower (1963), and Maxwell and Hower (1967). Nevertheless, a 2M dioctahedral mica was not unequivocally recognized in the samples studied here.

Chlorite. XRD analyses of < 2-μm fraction samples previously heated at 600° C for one hour revealed small amounts of chlorite in all samples. Chlorite was not detected in identically treated < 0.1-μm fraction samples until a well temperature of 194° C was reached. We interpret this to mean that chlorite recognized in the < 2-μm fraction at temperatures less than 194° C is detrital. The alternative leads to the unreasonable conclusion that chlorite forms preferentially in the coarser size fraction. Based on this argument we suggest that diagenetic chlorite forms in the Colorado River delta sediments between 180° C, the temperature of the deepest sample in which chlorite was not recognized in the < 0.1-μm fraction, and 194° C.

The appearance of diagenetic chlorite in this temperature range agrees with the results reported by several other workers in the Salton Trough (McDowell and Elders, 1980; Muffler and White, 1969). Nadeau and Reynolds (1981) note that in contact zones in the Mancos Shale the first appearance of chlorite is associated with R3 ordered illite-smectites at or near a calculated 200° isotherm.

Chlorite is a common constituent of the < 2-μm fraction of every sample above 194° C but is not detected above approximately 270° C in the < 0.1-μm fraction. We suspect that that relationship reflects an increase in grain size with chlorite recrystallization and the formation of idioblastic grains at temperatures near 300° C as reported by McDowell and Elders (1980).

Interference from illite reflections prevented determination of chlorite polytypes (Hayes, 1970).

Kaolinite. In the Borchard samples kaolinite is present in both the < 2-μm and the < 0.1-μm fractions. Although this kaolinite may be partly detrital, SEM examination of fine-grained sandstones from selected sample intervals reveals authigenically textured kaolinite. We presume that some kaolinite present in the mudrocks is authigenic as well. Kaolinite persists to temperatures at least as high as 210° C.

The possibility of detrital kaolinite in the < 0.1-μm fraction makes it difficult to determine at what temperature authigenic kaolinite is first formed. One approach is to assume that growth of authigenic kaolinite will increase the relative proportion of kaolinite in a sample and will therefore increase the relative intensity of the 7Å kaolinite peak. Since kaolinite is a significantly smaller part of the < 0.1-μm fraction than of the < 2-μm fraction the increase in intensity due to authigenic kaolinite should be most pronounced in < 0.1-μm

samples. In addition, below 194° C there is no interference from the second order chlorite peak in the < 0.1-μm fraction.

We determined the percentage of kaolinite in the < 0.1-μm fraction of selected samples according to the methods presented by Schultz (1964). Figure 3 plots these percentages against well temperature. Due to interference from the second order chlorite peak Figure 3 is not plotted for temperatures above 194° C.

The inflection at 105° C may represent the first appearance of kaolinite. It may also represent an increase in detrital kaolinite. Authigenically textured kaolinite is, however, displayed under SEM examination of fine-grained sandstones from sampled intervals above 105° C.

The last appearance of kaolinite overlaps the first appearance of chlorite. Boles and Franks (1979) report a similar distribution in Wilcox Group sandstones and suggest that a reaction relationship between the two minerals is indicated.

Potassium Feldspar. XRD analysis of randomly oriented > 2-μm fraction samples provides a semi-quantitative overview of non-clay minerals encountered in the Borchard wells. Figure 4 displays the results of these analyses.

Potassium feldspar decomposition is thought to be the primary source of the potassium and aluminum required by the smectite to illite conversion reaction (Hower et al., 1976). Variations in the amount of potassium feldspar are, therefore, of particular interest.

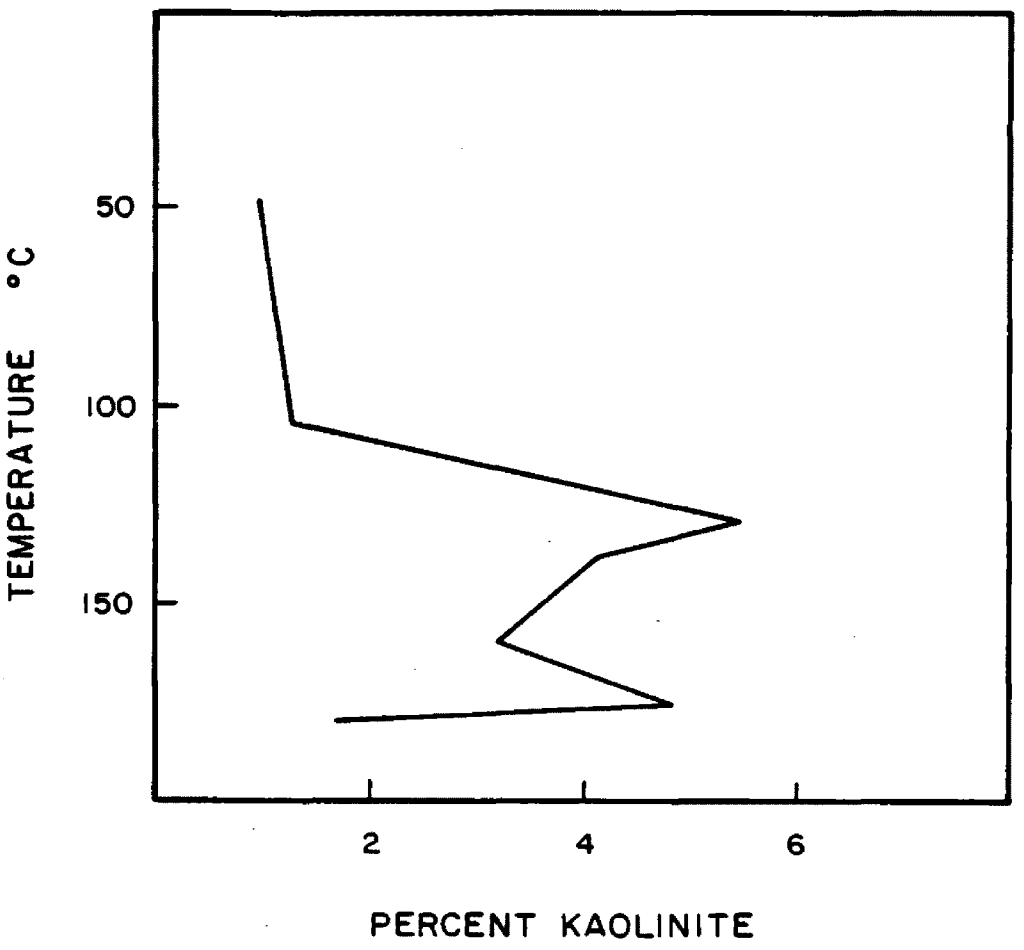


Figure 3. Kaolinite percentages plotted against logged well temperature, Borchard A-2.

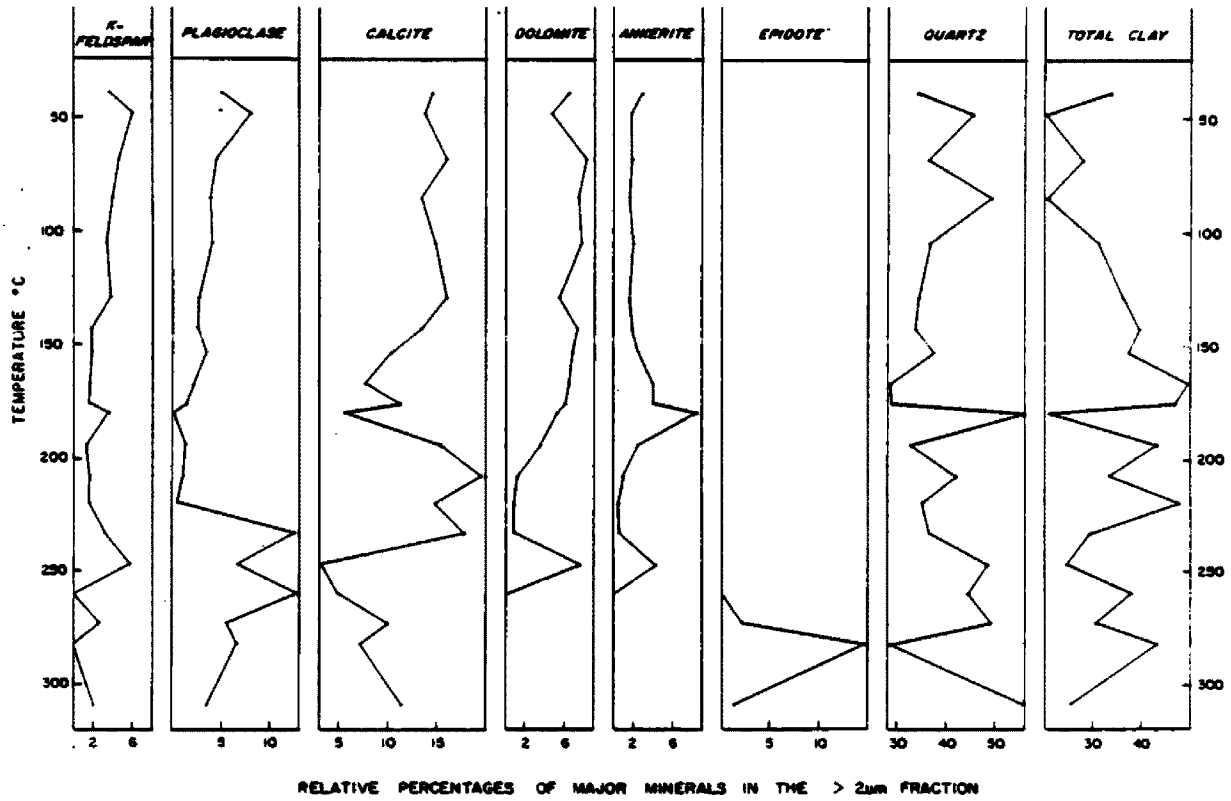


Figure 4. Mineralogy of the < 2-µm fraction of samples from Borchard A-2 and Borchard A-1 plotted against logged well temperature. Percentage values represent mineral proportions normalized to 100%. The method (Schultz, 1964) gives only semi-quantitative results. Percentage values in this figure serve only to indicate trends.

As Figure 4 illustrates, potassium feldspar decreases in abundance as temperature increases. The decrease in the amount of detrital potassium feldspar takes place over the same temperature interval as the smectite to illite conversion reaction, strong evidence that decomposition of feldspar does contribute to the illitization reaction.

Recent work in Gulf Coast sediments demonstrates that massive albitization of potassium feldspar is an important reaction that contributes significantly to the progressive loss of potassium feldspar with increasing depth (Land and Milliken, 1981). Muffler and White (1969) report that potassium feldspar and albite co-exist at temperatures above 300° C in the Salton Sea Geothermal Field. It is not clear what relationship exists between the albitization process and the formation of secondary potassium feldspar above 230° C as suggested by Figure 4.

## Compositional Variations

Whole-rock analysis of samples from the Borchard wells indicates no systematic change in chemical composition of the bulk sediments as depth and temperature increase. Table 2 displays weight percents of oxides of the constituent elements of the bulk samples. Figure 5 graphically represents the weight percent of the major oxides from Table 2 as a function of temperature. Variations in the weight percent of the major oxides above about 160° C reflect an increase in the frequency of occurrence of sandy interbeds and a concomitant increase in quartz.

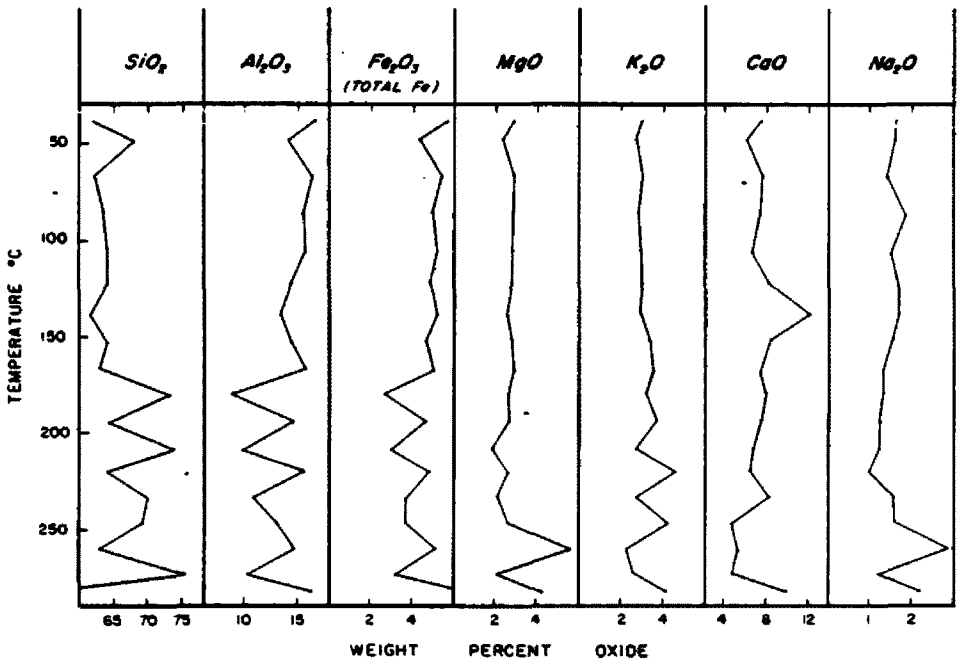


Figure 5. Major element concentrations from whole-rock analysis, Borchard A-2, plotted against logged well temperature.

TABLE 2. WHOLE ROCK ANALYSES OF BORCHARD A-2 SAMPLES

| | Oxide | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $TiO_2$ | $Fe_2O_3$ | FeO | MnO | CaO | MgO | $K_2O$ | $Na_2O$ | $P_2O_5$ | |
| Temp. °C | | | | | | | | | | | | Total |
| 39° | 61.84 | 16.54 | 0.71 | 2.60 | 2.98 | 0.07 | 7.50 | 2.94 | 2.98 | 1.64 | 0.19 | 99.99 |
| 48° | 68.09 | 14.12 | 0.51 | 2.01 | 2.30 | 0.07 | 6.06 | 2.39 | 2.69 | 1.60 | 0.15 | 99.99 |
| 68° | 62.18 | 16.40 | 0.70 | 2.55 | 2.92 | 0.07 | 7.60 | 2.94 | 3.02 | 1.42 | 0.19 | 99.99 |
| 85° | 63.54 | 15.69 | 0.68 | 2.32 | 2.66 | 0.08 | 7.32 | 2.87 | 2.80 | 1.85 | 0.18 | 99.99 |
| 105° | 64.07 | 15.87 | 0.64 | 2.40 | 2.75 | 0.08 | 6.71 | 2.81 | 3.02 | 1.48 | 0.17 | 100.00 |
| 122° | 64.15 | 14.42 | 0.62 | 2.27 | 2.61 | 0.07 | 8.11 | 2.80 | 3.05 | 1.70 | 0.20 | 100.00 |
| 138° | 61.54 | 13.15 | 0.53 | 2.38 | 2.73 | 0.17 | 12.18 | 2.52 | 2.92 | 1.70 | 0.18 | 100.00 |
| 152° | 63.98 | 14.28 | 0.66 | 2.15 | 2.47 | 0.07 | 8.43 | 2.80 | 3.39 | 1.54 | 0.21 | 99.98 |
| 167° | 62.97 | 15.91 | 0.67 | 2.43 | 2.68 | 0.09 | 7.37 | 2.94 | 3.53 | 1.29 | 0.21 | 100.00 |
| 180° | 73.10 | 8.56 | 0.39 | 1.22 | 1.40 | 0.07 | 8.01 | 2.60 | 3.19 | 1.33 | 0.14 | 100.01 |
| 194° | 64.36 | 14.81 | 0.60 | 2.19 | 2.51 | 0.08 | 7.58 | 2.70 | 3.72 | 1.24 | 0.18 | 99.97 |
| 208° | 73.85 | 9.84 | 0.47 | 1.40 | 1.60 | 0.06 | 6.90 | 1.79 | 2.70 | 1.23 | 0.16 | 100.00 |
| 220° | 63.94 | 15.71 | 0.62 | 2.21 | 2.53 | 0.08 | 6.43 | 2.68 | 4.63 | 0.99 | 0.19 | 100.01 |
| 233° | 70.09 | 10.86 | 0.49 | 1.72 | 1.97 | 0.06 | 8.20 | 2.17 | 2.69 | 1.57 | 0.17 | 99.99 |
| 247° | 69.19 | 13.01 | 0.50 | 1.72 | 1.98 | 0.13 | 4.81 | 2.60 | 4.31 | 1.61 | 0.14 | 100.00 |
| 260° | 63.14 | 14.85 | 0.73 | 2.39 | 2.74 | 0.04 | 5.13 | 5.63 | 2.26 | 2.39 | 0.19 | 99.99 |
| 273° | 75.63 | 10.00 | 0.40 | 1.50 | 1.71 | 0.06 | 4.80 | 2.02 | 2.54 | 1.22 | 0.12 | 100.00 |
| 282° | 55.57 | 16.47 | 0.77 | 2.98 | 3.41 | 0.09 | 9.99 | 4.18 | 4.10 | 2.22 | 0.23 | 100.01 |
| Analytical Precision | | | | | | | | | | | | |
| | 0.55 | 0.31 | 0.05 | 0.35 | -- | 0.01 | 0.22 | 0.15 | 0.03 | 0.16 | 0.014 | |
| Ignited Basis | | | | | | | | | | | | |

Table 3 displays the chemical compositions of the < 0.1-μm fraction of Borchard A-2 samples as a function of temperature. Table 3a represents the absolute weight percent of the oxides and Table 3b, the percentages normalized on a CaO-free basis.

Based on the progressively lower cation exchange capacity of increasingly illitic mixed-layer illite-smectites and the extremely low calcium values reported for most illites (Hower and Mowatt, 1966). we feel it is unlikely that calcium is a significant component of the clay fraction. Normalization of the weight percent oxides on a CaO-free basis eliminates the effect of variable proportions of calcium-bearing phases such as calcite and gypsum. This serves to clarify the representation of cation distribution in the silicate phases.

After normalization the weight percent oxides of the major elements were plotted against temperature (Figures 6 and 7). Unlike the whole rock samples, the < 0.1-μm fraction samples display significant trends as a function of increasing depth and temperature.

Over the interval containing the smectite to illite reaction $SiO_2$ shows a marked decrease while $Al_2O_3$ in the < 0.1-μm fraction increases (Figure 6). Over the same interval $K_2O$ increases dramatically while $Fe_2O_3$ (total Fe) and MgO decrease (Figure 7). $Na_2O$ values are included in the tables but, due to the addition of a small amount of Calgon to clay/water suspensions as a peptizing agent, their accuracy is questionable. In addition, the presence of Calgon almost certainly affects $P_2O_5$ values in the bulk sample analyses.

TABLE 3a WEIGHT PERCENT OF MAJOR OXIDES
BORCHARD A-2 SAMPLES, < 0.1-μm FRACTION

| | Oxide | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$* | MgO | $K_2O$ | CaO | $Na_2O$ | | |
| Temp. °C | | | | | | | | Total | Sample Mass mg |
| 39° | 49.35 | 20.82 | 9.50 | 3.49 | 2.68 | 2.77 | 1.22 | 89.83 | 40.14 |
| 48° | 58.12 | 20.71 | 7.93 | 3.53 | 2.65 | 2.68 | 0.82 | 96.44 | 80.71 |
| 68° | 57.78 | 20.57 | 7.29 | 3.80 | 2.78 | 5.52 | 0.46 | 98.20 | 20.12 |
| 85° | 57.43 | 21.41 | 8.45 | 3.60 | 2.71 | 3.79 | 0.68 | 98.07 | 40.13 |
| 105° | 63.00 | 23.74 | 6.56 | 3.78 | 2.92 | 1.01 | N.D. | 101.01 | 100.30 |
| 122° | 56.89 | 21.39 | 6.35 | 3.64 | 3.60 | 4.42 | 1.17 | 97.46 | 40.16 |
| 129° | 54.87 | 21.97 | 5.91 | 3.55 | 4.13 | 6.27 | 1.06 | 97.76 | 100.40 |
| 138° | 48.11 | 20.09 | 4.45 | 3.04 | 4.23 | 10.18 | 1.42 | 91.52 | 10.40 |
| 143° | 52.59 | 23.41 | 5.30 | 3.02 | 4.94 | 3.43 | 1.65 | 94.34 | 100.40 |
| 153° | 52.56 | 25.03 | 3.32 | 2.27 | 6.08 | 3.96 | 1.40 | 94.62 | 40.32 |
| 160° | 46.47 | 21.78 | 3.49 | 2.16 | 6.62 | 8.26 | 4.33 | 93.11 | 40.73 |
| 167° | 49.34 | 22.82 | 3.64 | 2.48 | 5.69 | 6.38 | 3.33 | 93.68 | 20.33 |
| 176° | 48.48 | 24.56 | 3.21 | 2.70 | 6.52 | 6.41 | 3.51 | 95.39 | 99.10 |
| 180° | 45.62 | 22.39 | 2.02 | 2.52 | 6.24 | 10.80 | 3.24 | 92.83 | 20.54 |
| 194° | 41.46 | 19.31 | 3.06 | 2.84 | 4.31 | 17.29 | 0.30 | 88.57 | 10.96 |
| 208° | 45.27 | 21.89 | 3.34 | 3.13 | 5.94 | 11.20 | 3.14 | 93.91 | 40.15 |
| 220° | 37.58 | 17.93 | 2.25 | 3.53 | 5.33 | 25.00 | N.D. | 91.62 | 7.572 |
| 233° | 44.05 | 15.02 | 2.56 | 4.41 | 3.11 | 20.47 | 9.31 | 98.93 | 3.135 |
| **260° | -1.40 | -2.42 | N.D. | 0.76 | 0.35 | 38.43 | 0.36 | 43.72 | 19.85 |
| 273° | 24.33 | 9.72 | 1.13 | 2.73 | 2.50 | 36.23 | 0.81 | 77.45 | 10.92 |
| **282° | -2.33 | -1.25 | N.D. | 1.46 | 0.69 | 38.29 | 2.41 | 46.43 | 40.07 |
| Max. error % of wt.% | 4.92 | 4.92 | 4.46 | 6.49 | 8.21 | 11.50 | 5.13 | | |

Ignited basis
* Total Fe reported as $Fe_2O_3$
** Sample is nearly pure gypsum in the < 0.1-μm fraction.
- Value falls outside stated maximum error.

TABLE 3b. WEIGHT PERCENT OF MAJOR OXIDES

BORCHARD A-2 SAMPLES, < 0.1-μm FRACTION, NORMALIZED, CaO-FREE

| | Oxide | | | | | | |
|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$* | MgO | $K_2O$ | $Na_2O$ | X |
| Temp. °C | | | | | | | |
| 39° | 52.91 | 22.32 | 10.19 | 3.74 | 2.87 | 1.31 | 6.66 |
| 48° | 61.99 | 22.09 | 8.46 | 3.76 | 2.83 | 0.87 | 0.00 |
| 68° | 62.34 | 22.19 | 7.87 | 4.10 | 3.00 | 0.50 | 0.00 |
| 85° | 60.91 | 22.71 | 8.96 | 3.82 | 2.87 | 0.72 | 0.00 |
| 105° | 63.00 | 23.74 | 6.56 | 3.78 | 2.92 | N.D. | 0.00 |
| 122° | 61.15 | 22.99 | 6.83 | 3.91 | 3.87 | 1.26 | 0.00 |
| 129° | 59.97 | 24.01 | 6.46 | 3.88 | 4.51 | 1.16 | 0.00 |
| 138° | 59.15 | 24.70 | 5.47 | 3.74 | 5.20 | 1.75 | 0.00 |
| 143° | 57.37 | 25.54 | 5.78 | 3.29 | 5.39 | 1.80 | 0.83 |
| 153° | 57.97 | 27.61 | 3.66 | 2.50 | 6.71 | 1.54 | 0.00 |
| 160° | 54.77 | 25.67 | 4.11 | 2.55 | 7.80 | 5.10 | 0.00 |
| 167° | 56.52 | 26.14 | 4.17 | 2.84 | 6.52 | 3.81 | 0.00 |
| 176° | 54.48 | 27.60 | 3.61 | 3.03 | 7.33 | 3.94 | 0.00 |
| 180° | 55.61 | 27.29 | 2.46 | 3.07 | 7.61 | 3.95 | 0.00 |
| 194° | 58.16 | 27.09 | 4.29 | 3.98 | 6.05 | 0.42 | 0.00 |
| 208° | 54.73 | 26.47 | 4.04 | 3.78 | 7.18 | 3.80 | 0.00 |
| 220° | 56.41 | 26.91 | 3.38 | 5.30 | 8.00 | N.D. | 0.00 |
| 233° | 56.14 | 19.14 | 3.26 | 5.62 | 3.96 | 11.87 | 0.00 |
| 273° | 59.02 | 23.58 | 2.74 | 6.62 | 6.07 | 1.97 | 0.00 |

Ignited basis.

* Total Fe reported as $Fe_2O_3$.

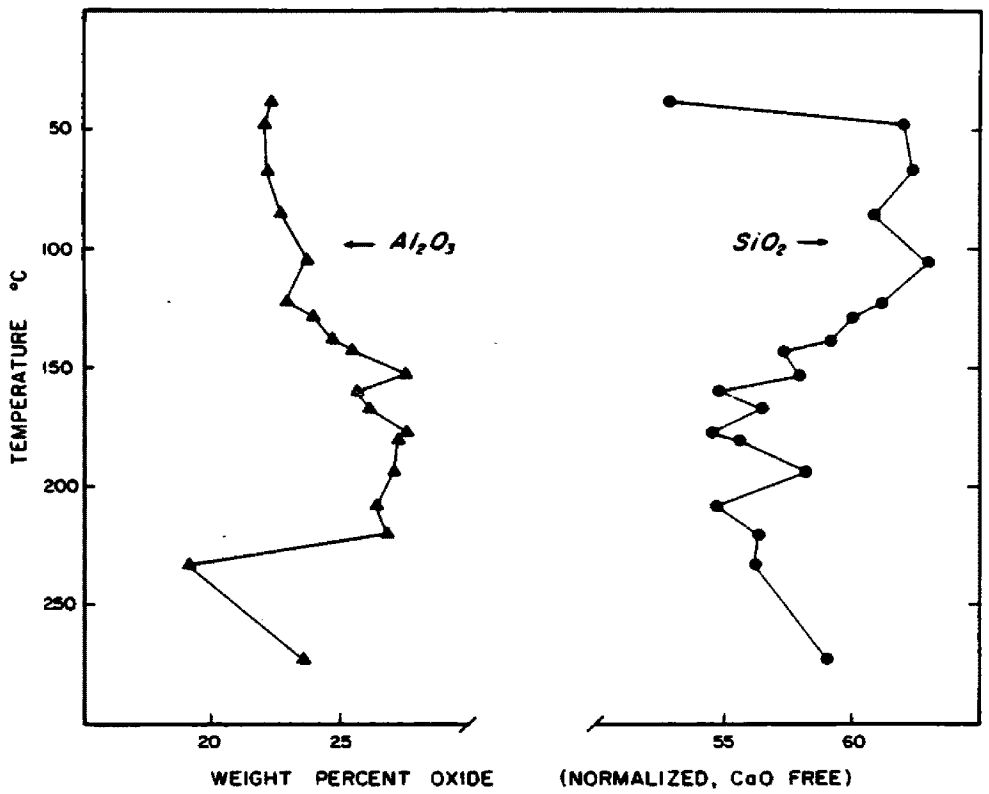


Figure 6. Weight percent $Al_2O_3$ and $SiO_2$ in the < 0.1-μm fraction of samples from Borchard A-2 plotted against logged well temperatures.

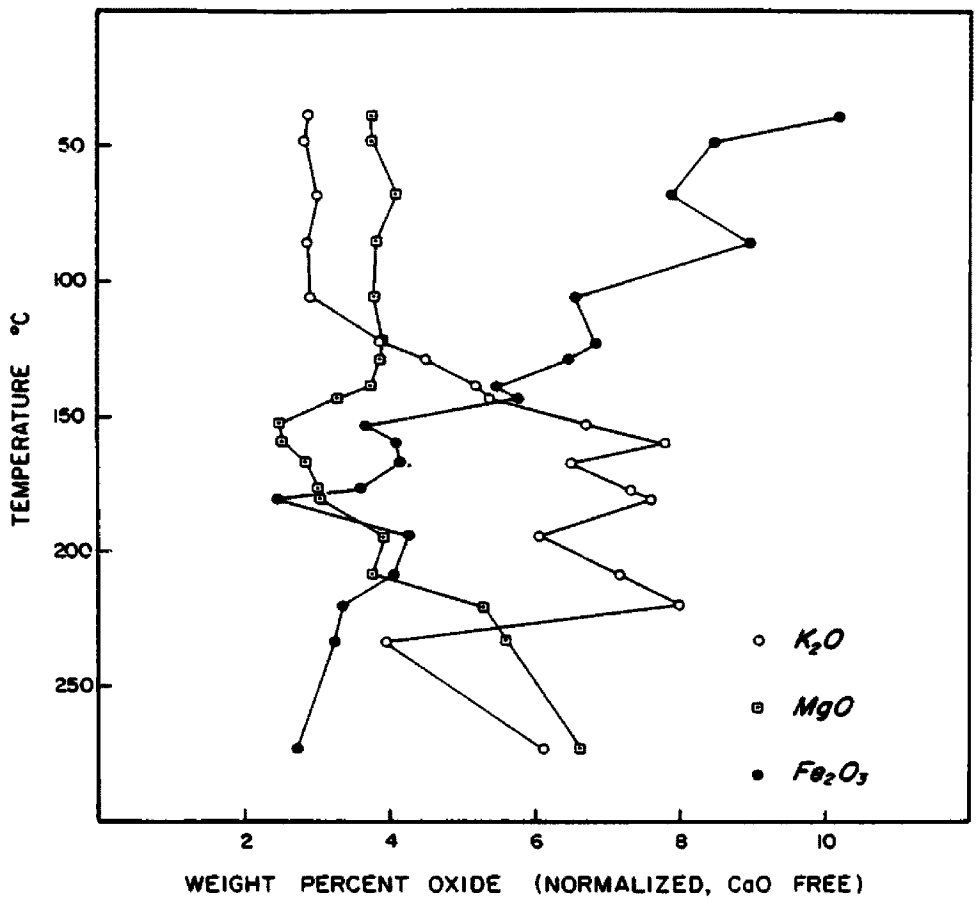


Figure 7. Weight percent $K_2O$, MgO, and $Fe_2O_3$ in the < 0.1-μm fraction of samples from Borchard A-2 plotted against logged well temperatures.

# DISCUSSION AND CONCLUSIONS

## Chemistry and Mineralogy

Several variables may influence the appearance of mineral assemblages in a burial sequence. Changes in depositional environment, provenance, tectonic setting, and climate may all contribute to a variation in detrital mineralogy over time. Migrating pore waters may introduce additional components that significantly affect reactions. In order to attribute the systematic mineralogic variations seen in burial sequences to an increase in depth and temperature it is necessary, if possible, to eliminate other possibilities or, failing that, to recognize the extent of their contributions.

An examination of cuttings and well logs indicates that the Borchard sections, particularly the low-temperature interval within which the illitization reaction takes place, are dominated by relatively impermeable mudrocks making large-scale migration of pore waters unlikely. Muffler and Doe's (1969) work indicates that lithology is essentially uniform throughout the section. Both substantial variations in original mineralogy and any significant addition of components from outside the system should be reflected in the chemical compositions of bulk samples. As Figure 5 illustrates, there are no systematic downhole compositional variations in the bulk samples.

The < 0.1-μm fractions of the same samples do, however, show compositional changes that vary as a function of increased depth and temperature, and parallel the mineralogical trends detected by XRD analysis.

Figures 6 and 7 display the major oxides plotted against well temperature. The overall trends, a decrease in $SiO_2$, $Fe_2O_3$, and MgO and an increase in $Al_2O_3$ and $K_2O$, are consistent with the general reaction presented by Hower et al. (1976): Smectite + K-spar = Illite + Chlorite + Quartz. In addition the figures portray the probable distribution of components within the clay minerals and illustrate the chemical exchange between the coarse fraction and the < 0.1-μm, clay-rich fraction.

Examination of the coarse fraction reveals a progressive decrease in the amount of potassium feldspar (Figure 4) over the same temperature interval within which the illitization reaction occurs (Figure 2). This implies redistribution of potassium and perhaps aluminum from feldspar in the coarse fraction to clay minerals in the fine fraction.

The systematic variations in chemical composition of the < 0.1-μm fraction parallel the mineralogic changes summarized in Figure 8.

Over the temperature interval 150° C to 220° C Figure 7 reveals an antipathetic relationship between the trends of MgO and $Fe_2O_3$ and the $K_2O$ trend in the < 0.1-μm fraction. Over the same interval $SiO_2$ content of the < 0.1-μm fraction varies antipathetically with $Fe_2O_3$ and MgO content (Figure 6).

XRD analysis indicates that the temperature interval 180° C to 194° C brackets the first appearance of diagenetic chlorite. Over this interval Figures 6 and 7 show a sharp increase in $Fe_2O_3$, MgO, and $SiO_2$ content and a corresponding decrease in $K_2O$ content. This is the

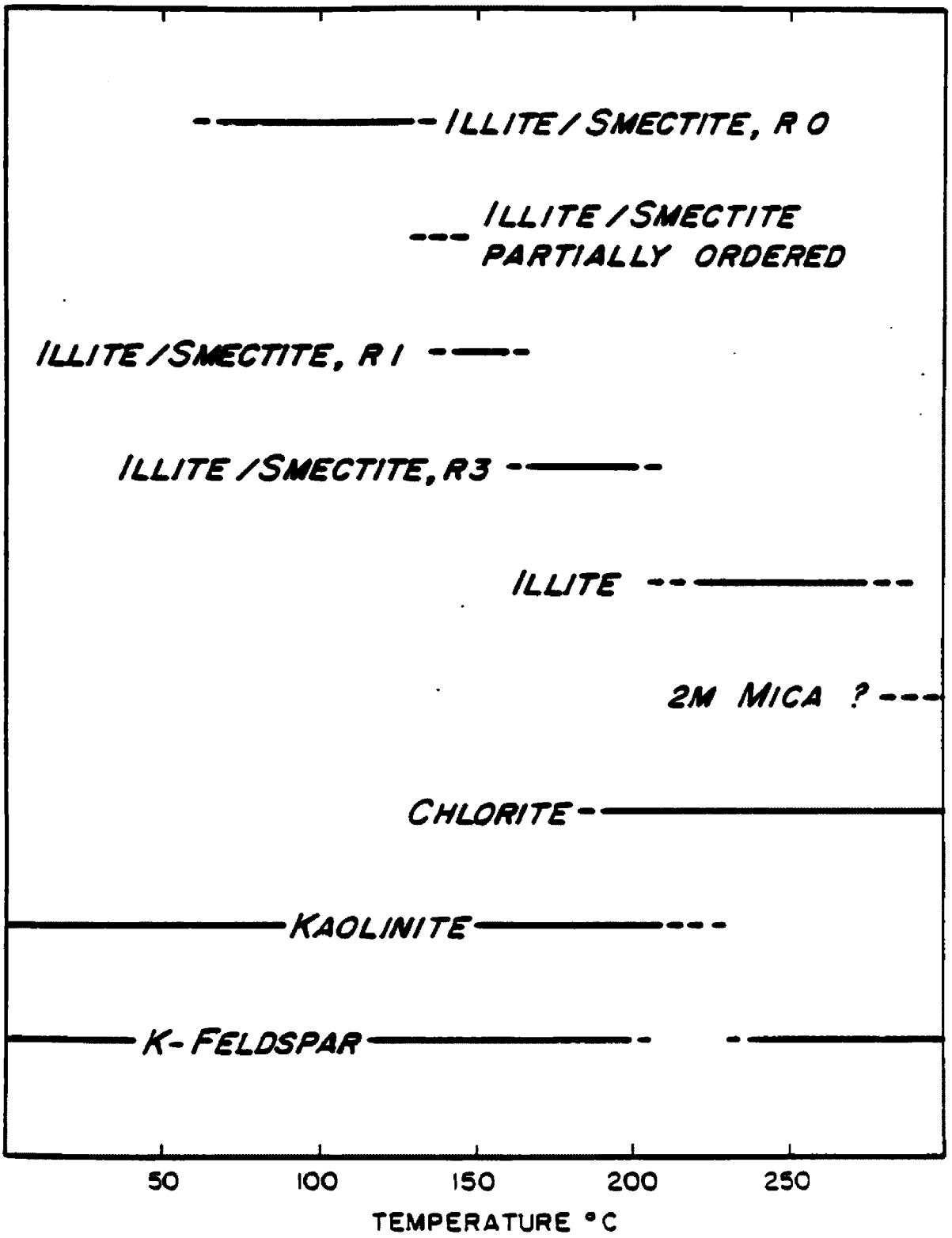


Figure 8. Mineralogy vs. logged well temperatures, Borchard A-2.

response that should result from an introduction of chlorite into the < 0.1-μm fraction.

The subsequent steady increase in MgO and the decrease in $Fe_2O_3$ at temperatures above 210° C (Figure 7) may reflect changing chlorite composition. McDowell and Elders (1980) report that chlorite in the Salton Sea Geothermal Field becomes increasingly magnesium-rich as temperature increases. Chlorites in the Brawley field may follow the same trend; if so that will be reflected in the chemical analyses of the < 0.1-μm fraction as increasing MgO and decreasing $Fe_2O_3$.

Compositional trends in the temperature interval 155° C to 166° C mimic those associated with the first appearance of diagenetic chlorite. XRD analysis, however, reveals no chlorite. This may reflect the intermittent occurrence of diagenetic chlorite at levels below the limits of detection of XRD techniques.

Throughout most of the course of the illitization reaction MgO content of the < 0.1-μm fraction remains unchanged. But at the point where the arrangement of smectite and illite layers changes from a random configuration to an ordered one MgO rapidly decreases. The rate of decrease in $Fe_2O_3$ appears to accelerate over this same interval. This may reflect compositional variation in the smectite layers of the original, detrital, mixed-layer clays. Boles and Franks (1979) suggest that until the onset of ordering aluminous smectites react more readily to form illite than do iron and magnesium-rich smectites. As a result the unreacted smectite component of the mixed-layer clays is progressively

enriched in iron and magnesium. The maintenance of high MgO values coincident with an RO configuration and the sudden loss of MgO at the onset of R1 ordering is compatible with this interpretation.

$Al_2O_3$ content in the < 0.1-μm fraction of the Borchard A-2 samples increases downhole until a well temperature of approximately 175° C is reached. Very little variation is apparent between 175° C and 220° C. Over most of this temperature interval (up to 194° C) the < 0.1-μm fraction is composed of mixed-layer illite-smectite and subordinate amounts of kaolinite. The initial increase in $Al_2O_3$ can be attributed to the tetrahedral substitution of aluminum for silicon in the mixed-layer clays. It may also represent, at least in part, the growth of diagnetic kaolinite.

In order to fix potassium in the interlayer position of smectite and thus form illite a net negative charge of 0.7-0.8 on the smectite 2:1 layer must be achieved (Hower and Mowatt, 1966). If this is accomplished entirely by tetrahedral substitution of aluminum for silicon the amount of aluminum required to create the net negative charge is approximately half the amount of the potassium required to balance it. Even if potassium feldspar is the only source of the potassium and aluminum required by the illitization reaction nearly half the aluminum in the feldspar is left over after that reaction is complete. This excess aluminum is then available for use by other aluminous phases such as kaolinite and chlorite. As the following reaction demonstrates it is possible to form illite and kaolinite

simultaneously from the products of potassium feldspar decomposition.

$$20\left[(X^{+1}_{0.3})(Al_{1.85}\,Mg_{0.15})(Si_{3.85}Al_{0.15})\,O_{10}(OH)_2\right] + 16KAlSi_3O_8$$

$$+ 10H_2O =$$

$$20\left[(K_{0.8})(Al_{1.85}Mg_{0.15})(Si_{3.35}Al_{0.65})\,O_{10}(OH)_2\right]$$

$$+ 3\,Al_2Si_2O_5(OH)_4 + 52\,SiO_2 + 6XOH + H_2O$$

If octahedral substitution of divalent cations for trivalent octahedral aluminum also contributes to the increase in net negative charge on the smectite 2:1 layer, greater amounts of kaolinite and lesser amounts of quartz are formed.

In summary, the illitization reaction and perhaps the formation of kaolinite appear to proceed at the expense of potassium-bearing phases, particularly potassium feldspar, in the coarse size fraction. Growth of diagenetic chlorite is associated with the breakdown of kaolinite and the release of magnesium and iron from smectite layers. Redistribution of components within an essentially closed system appears to be the best explanation for the relationship between bulk composition, fine-fraction composition, and mineralogy.

## Kinetic Considerations

Hower et al. (1976) compared variations in chemical composition of Recent through Paleozoic shales with the changes produced by burial metamorphism in two middle Tertiary, Gulf Coast sequences. The

resulting plots of major oxide abundances are strikingly similar. Mineralogic trends in the Gulf Coast burial sequences also parallel the age-dependent variations seen in shales. Hower et al. (1976) concluded that the mineralogic and chemical compositions of older shales result from the same metamorphic processes that produce the systematic trends seen in single burial sequences in the Gulf Coast. Given enough time all shale sequences will exhibit the illite-chlorite assemblage seen in sediments subjected to burial metamorphism.

The burial metamorphic sequence seen in the Colorado River delta sediments is the result of an anomalously high geothermal gradient, a high sedimentation rate, and very young age. Figure 9 compares illite percentages in the < 0.1-μm fraction of samples from C.W.R.U. #6 well (data from Hower et al., 1976) with illite percentages in the < 0.1-μm fraction of samples from Borchard A-2. It is immediately apparent that higher temperatures are required for the illitization reaction to occur in Plio-Pleistocene sediments than for the same reaction to occur in Tertiary sequences. Hower et al. (1976) and Hoffman and Hower (1979) discuss the importance of reaction times in determining the appearance of particular mineral assemblages in a burial metamorphic sequence. Figure 9 confirms that, at low temperatures, geologic age significantly influences the mineralogy of mixed-layer illite-smectite over nearly the full range of the illitization reaction. Lack of illite percentages above about 80 percent in the Tertiary sequences prevents comparison beyond that point.

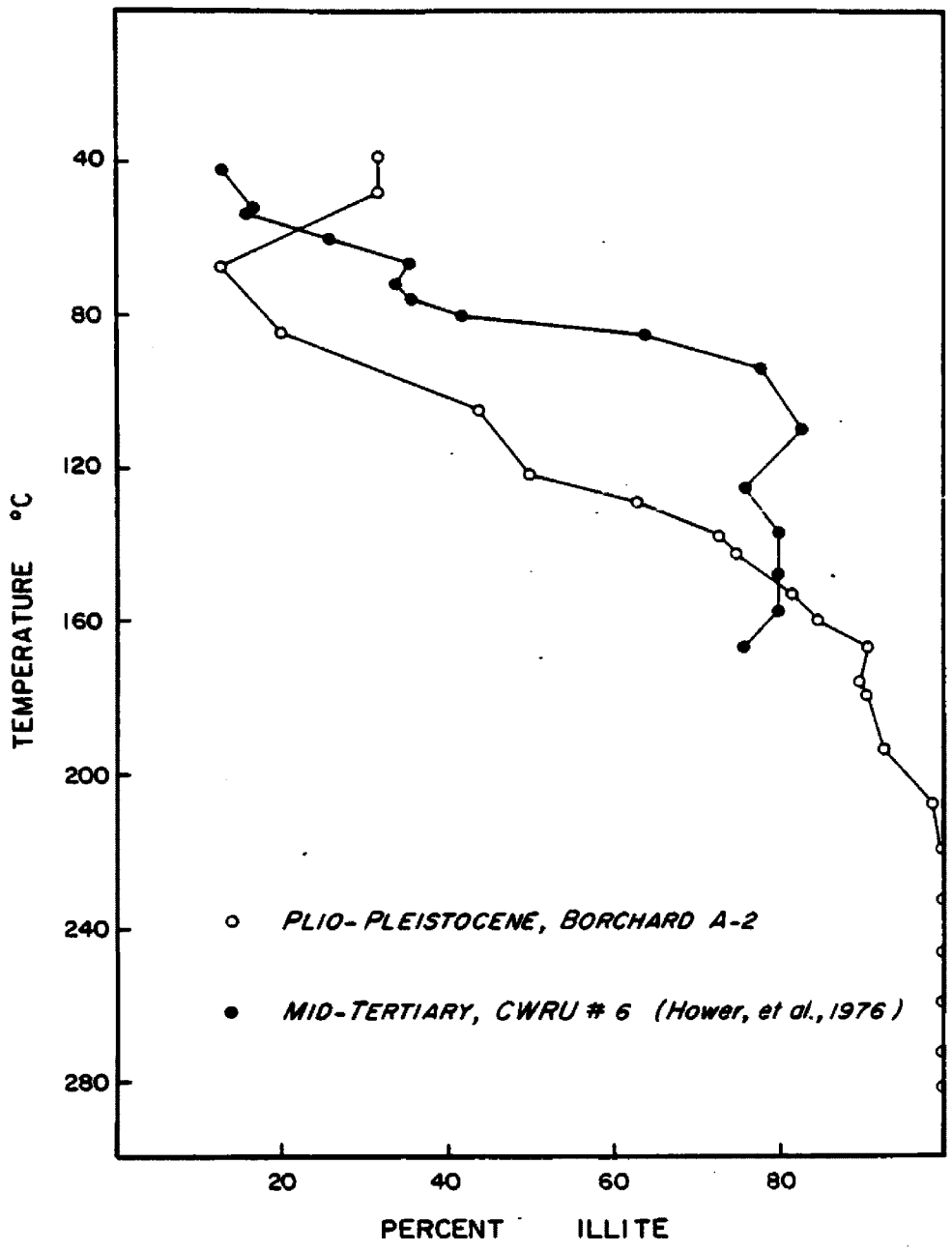


Figure 9. Comparison of percent illite layers in the < 0.1-μm fraction of samples from the Plio-Pleistocene, Borchard A-2 wells with the Mid-Tertiary CWRU #6 well (Hower et al. 1976). Data plotted against logged well temperatures.

We are currently involved in a detailed investigation of the kinetics of the illitization reaction. That study will be the subject of a future paper.

Hoffman and Hower (1979) compiled temperatures associated with metamorphic grade changes in Lower Tertiary/Upper Mesozoic shale sequences. Their metamorphic grade changes are presented in Figure 10. The present study documents similar grade changes in much younger rocks. Table 4 presents a comparison of temperatures associated with the grade changes for Lower Tertiary/Upper Mesozoic rocks (Hoffman and Hower, 1979) with corresponding temperatures for Plio-Pleistocene sediments from this study.

The data in Table 4 indicates that at temperatures of approximately 160° C and above, in rocks of Plio-Pleistocene age and older, geologic age is no longer important in determining mineral assemblage. At temperatures below 160° C geologic age and temperature combine to determine mineral assemblage.

## SUMMARY OF CONCLUSIONS

1. Mixed-layer illite-smectites become increasingly illitic with increasing temperature until pure illite is formed at about 210° C.
2. Chlorite probably appears as a diagenetic mineral between 180° C and 194° C. This temperature range is coincident with the onset of R3 ordering in illite-smectites.

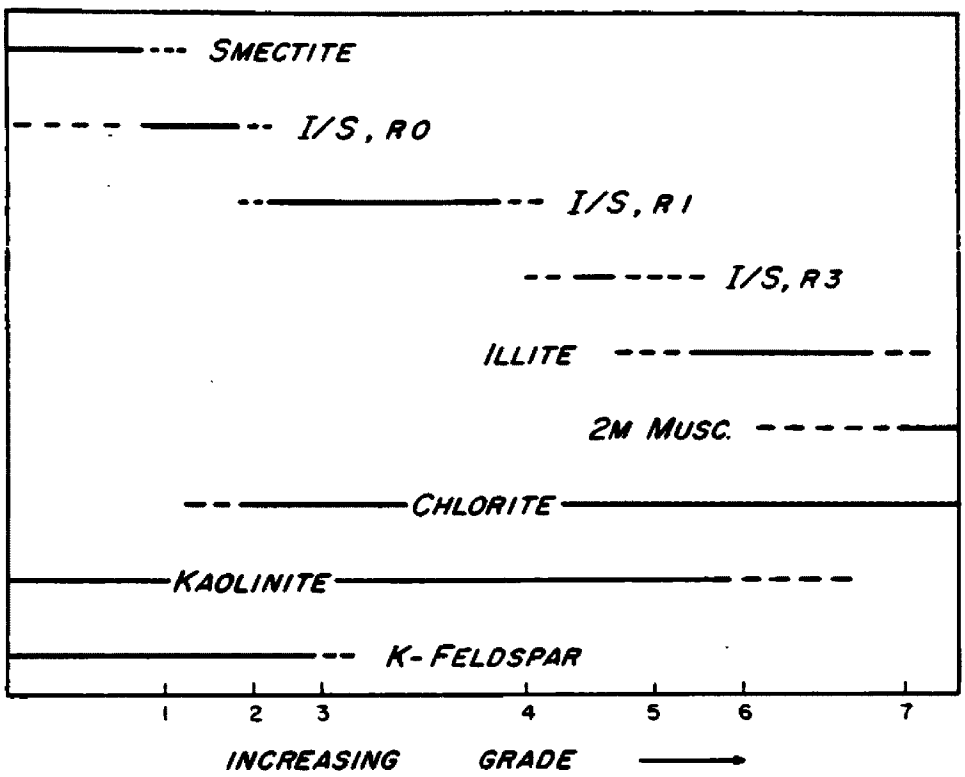


Figure 10. Metamorphic grades in pre-greenschist facies pelitic rocks (after Hoffman and Hower 1979, Figure 2).

TABLE 4. TEMPERATURE FOR GRADE CHANGES FROM FIGURE 10

| Grade | Upper Mesozoic/Lower Tertiary* Temp. °C | Plio-Pleistocene** Temp. °C |
|---|---|---|
| 1 | 60° | 68° |
| 2 | 100° | 140° |
| 3 | 120° | |
| 4 | 175° | 165° |
| 5 | 200° | 210° |
| 6 | --- | +210° |
| 7 | 300° | 300° |

* Hoffman and Hower (1979)

**Borchard A-2

3. Data from this paper and from the Gulf Coast studies (Hower et al., 1976) strongly suggests that potassium feldspar decomposition provides potassium and aluminum required by the illitization reaction and that the extent of the illitization reaction is determined by the availability of potassium feldspar.
4. The illitization reaction requires higher temperatures in Plio-Pleistocene sediments than in Tertiary sediments. This confirms that reaction rates are important in determining mineral assemblages at low temperatures.
5. Approximately 160° C appears to be a threshold temperature above which reaction rates cease to be important in determining clay mineral assemblage in rocks of Plio-Pleistocene age and older.

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